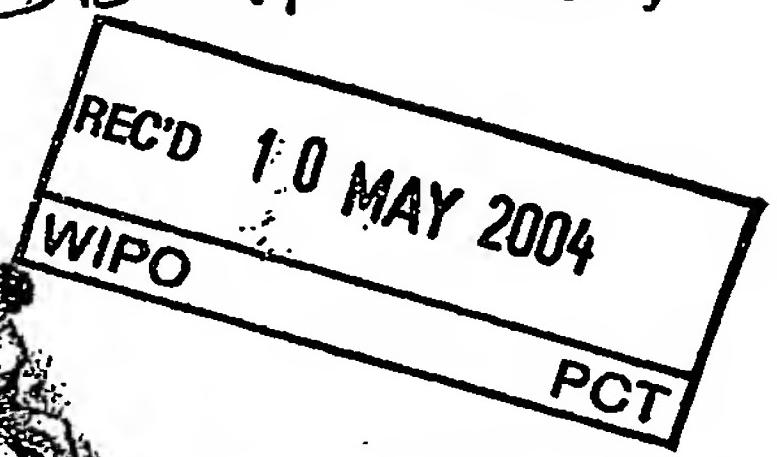


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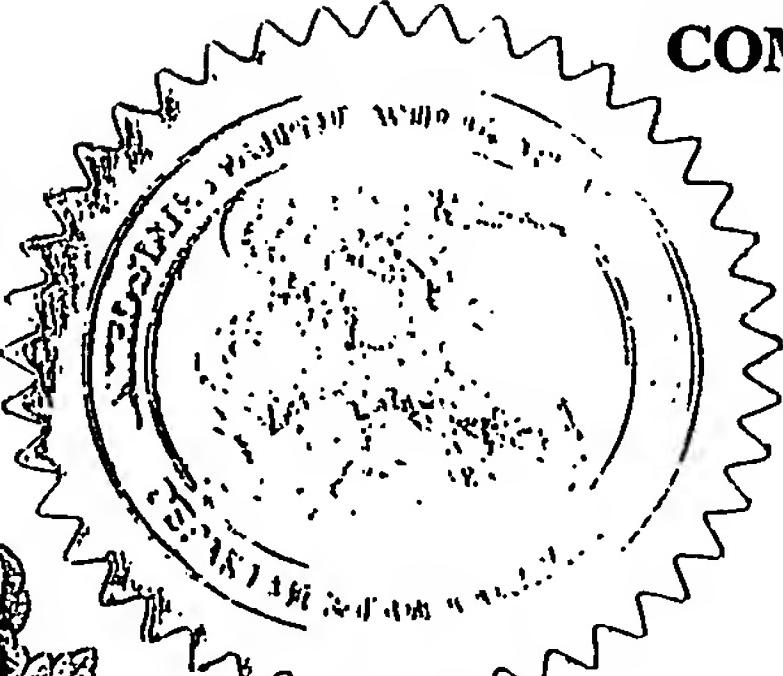
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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. EV 317506474 US

INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
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 Additional inventors are being named on the _____ separately numbered sheets attached hereto**TITLE OF THE INVENTION (500 characters max)**

Extraction Of Oxygenates From A Hydrocarbon Stream

Direct all correspondence to:

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OR

<input checked="" type="checkbox"/> Firm or Individual Name	Browning Bushman P.C.			
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ENCLOSED APPLICATION PARTS (check all that apply)

<input checked="" type="checkbox"/> Specification	Number of Pages	14	<input type="checkbox"/> CD(s), Number	_____
<input checked="" type="checkbox"/> Drawing(s)	Number of Sheets	1	<input type="checkbox"/> Other (specify)	_____
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76				

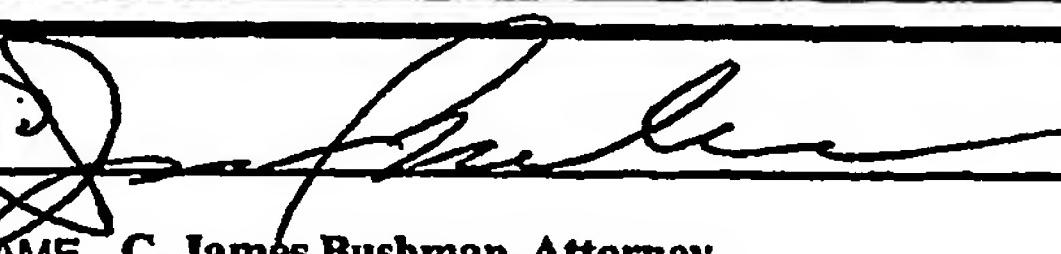
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Respectfully submitted,

SIGNATURE TYPED or PRINTED NAME C. James Bushman, AttorneyTELEPHONE 713-266-5593Date 08-21-03REGISTRATION NO.
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Docket Number:24,810Sasol S.A.-7**USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT**

This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop Provisional Application.

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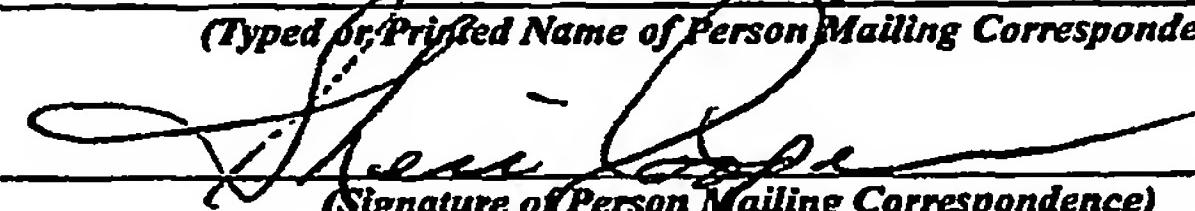
CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10)Applicant(s): **Johan Pieter de Wet, Wilhelmina Jansen and Paul Jacobson**

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EXTRACTION OF OXYGENATES FROM A HYDROCARBON STREAM

BACKGROUND OF THE INVENTION

This invention relates to a method for extracting oxygenates from a hydrocarbon stream.

Many methods for extracting oxygenates from hydrocarbon streams are known. Such extraction methods include hydrogenation, azeotropic distillation, extractive distillation, vapour phase dehydration, liquid phase dehydration and liquid-liquid extraction.

This invention relates to a process for extracting or separating oxygenates from the condensation product of a low temperature Fischer-Tropsch reaction, to produce a condensation product that is particularly suitable for the production of linear alkyl benzene.

SUMMARY OF THE INVENTION

According to the invention there is provided a method for extracting oxygenates from the condensation product of a low temperature Fischer-Tropsch reaction, while preserving the olefin content of the condensation product. The condensation product typically contains 15% to 30% by weight olefins, usually 15% to 25% by weight olefins, 60% to 80% by weight paraffins and 5% to 10% by weight oxygenates.

The oxygenate extraction process is a liquid-liquid extraction process that preferably takes place in an extraction column using a mixture of methanol

and water as the solvent, wherein an extract from the liquid-liquid extraction is sent to a solvent recovery column from which a tops product comprising methanol, olefins and paraffins is recycled to the extraction column, thereby enhancing the overall recovery of olefins and paraffins. A bottoms product from solvent recovery column may also be recycled to the extraction column.

The solvent preferably has a water content of more than 3% by weight, more preferably a water content of about 5% - 15% by weight.

Preferably, a raffinate from the extraction column is sent to a stripper column from which a hydrocarbon feed stream containing more than 85% by weight olefins and paraffins and typically less than 0.2% by weight, preferably less than 0.02% by weight by weight oxygenates exits as a bottoms product.

According to another aspect of the invention, the solvent recovery column includes an extract inlet, an upper overhead outlet and a lower bottoms outlet, with a side-draw located above the extract feed point and below the overheads outlet.

BRIEF DESCRIPTION OF THE DRAWING

The Figure is a block diagram of a process of the invention for extracting oxygenates from a hydrocarbon stream.

DESCRIPTION OF PREFERRED EMBODIMENTS

This invention relates to a process for extracting oxygenates from a hydrocarbon condensate stream from a low temperature Fischer-Tropsch reaction. The substantially oxygenate-free hydrocarbon stream can be used in the production of linear alkyl benzene.

In the Fischer-Tropsch process, synthesis gas (carbon monoxide and hydrogen) obtained either from the gasification of coal or the reforming of natural gas, is reacted over a Fischer Tropsch catalyst to produce a mixture of hydrocarbons ranging from methane to waxes and smaller amounts of oxygenates.

In a low temperature Fischer-Tropsch reaction, the reaction takes place in a slurry bed reactor or fixed bed reactor, preferably a slurry bed reactor, at a temperature in the range of 160°C - 280°C, preferably 210°C - 260°C, and a pressure in the range of 18-50 bar (gauge), preferably between 20-30 bar (gauge), in the presence of a catalyst. The catalyst may include iron, cobalt, nickel or ruthenium. However, a cobalt-based catalyst is preferred for the low temperature reaction. Usually, the cobalt catalyst is supported on an alumina support.

During the Fischer-Tropsch reaction, a lighter hydrocarbon vapour phase is separated from a liquid phase comprising heavier liquid hydrocarbon products. The heavier liquid hydrocarbon product (waxy products) is the major product of the reaction and may, for example, be hydrocracked to produce diesel and naphtha.

The lighter hydrocarbon vapour phase which comprises gaseous hydrocarbon products, unreacted synthesis gas and water is condensed to provide a "condensation product" which comprises an aqueous phase and a hydrocarbon condensation product phase.

The hydrocarbon condensation product includes olefins, paraffins in the C₄ to C₂₆ range, and oxygenates including alcohols, esters, aldehydes, ketones and acids.

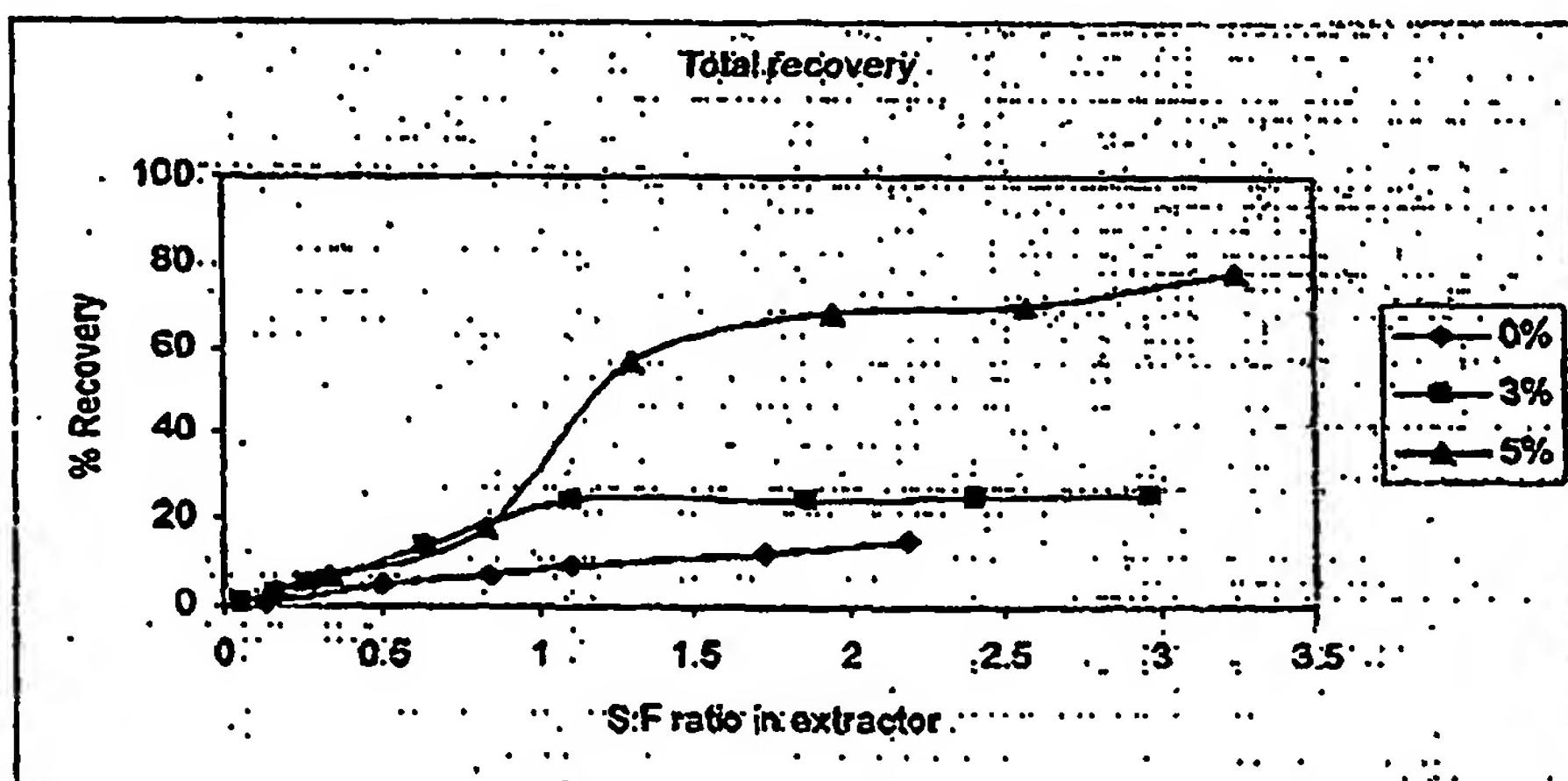
Typically, a hydrocarbon condensation product for a low temperature Fischer-Tropsch reaction contains 15%-30% by weight olefins, 60%-80% by weight paraffins, and 5%-10% by weight oxygenates. It has, surprisingly, been found that even though this condensation product has a low olefin

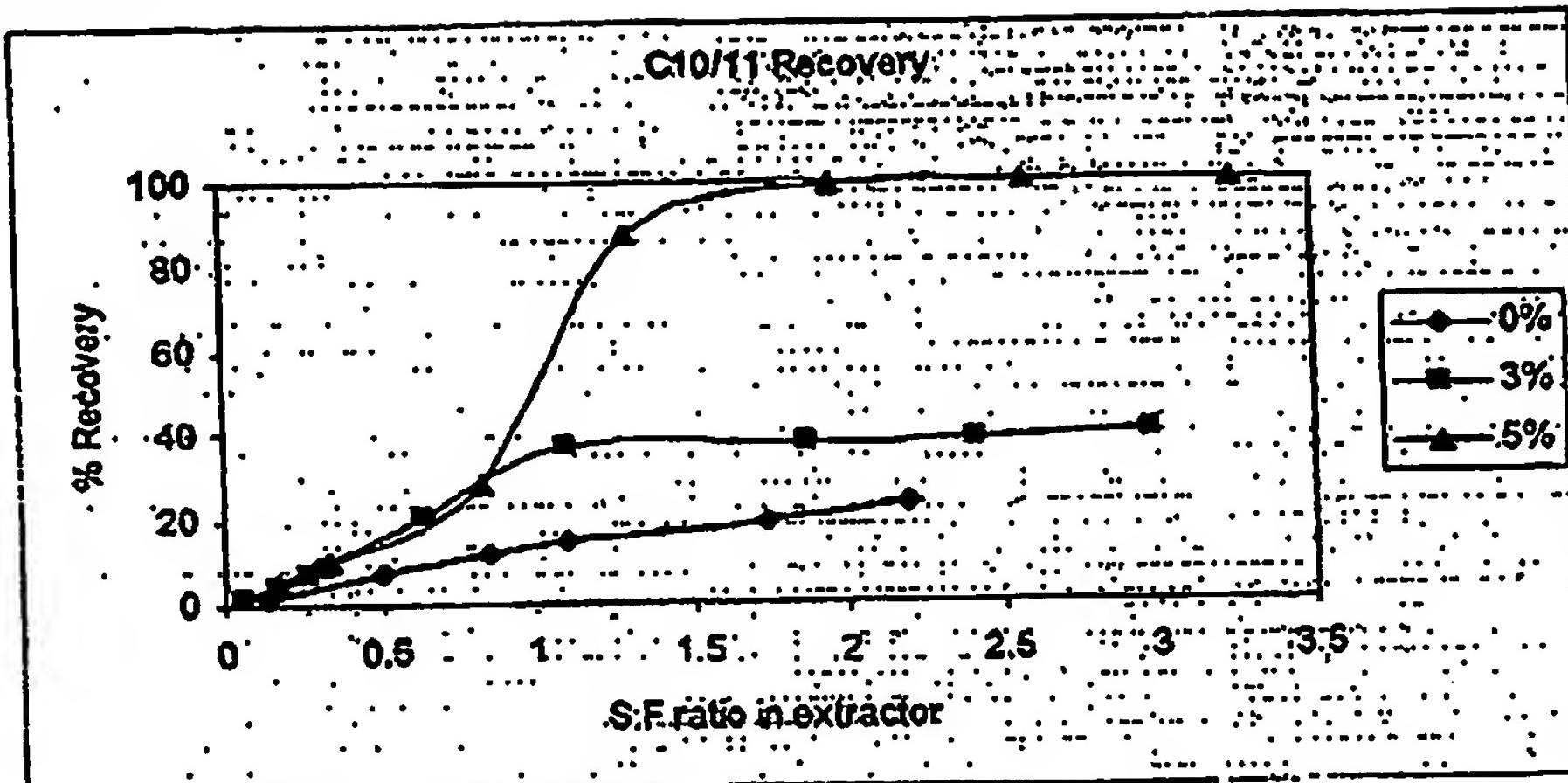
content, it can be used in the production of linear alkyl benzene. However, it is necessary to first extract the oxygenates as these species have a negative effect on the alkylation reaction. There is therefore a need to find a process for extracting oxygenates, but at the same time preserve the olefin concentration. For the production of linear alkyl benzene, the hydrocarbon condensate product is fractionated into a C₁₀ – C₁₃ cut which, by way of example, contains 25% by weight olefins, 68% by weight paraffins and 7% by weight oxygenates.

In the prior art, many methods of extracting oxygenates from hydrocarbon streams are suggested. Such removal methods include hydrogenation, azeotropic distillation, extractive distillation, vapour phase dehydration, liquid phase dehydration and liquid-liquid extraction. It has been found that liquid-liquid extraction is a preferred method of oxygenate extraction because, if the correct solvent is selected, the olefin concentration can be preserved. In liquid-liquid extraction, the solvent can be any polar material that has partial miscibility with the feed stream 14, such as tri-ethanol amine, tri-ethylene glycol with between zero and 20% water, acetonitrile with between 5% and 20% water, acetol, diols, methanol, or ethanol and water. Normally, a high-boiling point solvent is preferred because the solvent recovery steps after extraction require less energy than will be the case for a low-boiling point solvent. However, it has been found that a mixture of methanol and water, which is a low-boiling point solvent, need not suffer from this drawback, because it can be effective at low solvent to feed ratios (this can be lower than 1 if the required oxygenate extraction is not too severe). Furthermore, one would not expect to be able to use methanol and water as a solvent in a liquid-liquid extraction column to extract oxygenates from the abovementioned hydrocarbon condensate because a study of the different azeotropes with water that exist in the hydrocarbon condensate would lead one to expect that it would not be possible to distil water in a solvent recovery column without azeotroping oxygenates overhead as well. Surprisingly, this turns out not to be the case.

A further aspect of the invention is that it has been found that a water/methanol solvent, preferably with greater than 3% by weight water content in the liquid-liquid extraction column leads to better recovery of desired products in the solvent recovery column than a dry methanol solvent or a water/methanol solvent with less than 3% by weight water in the liquid-liquid extraction column. This is shown in Graph 1 below, from which it can be seen that a methanol/water solvent with 5% by weight water provides over 80% recovery of olefins and paraffins in the solvent recovery column. Graph 2 below shows that almost a 100% recovery of C10/C11 olefins and paraffins in the solvent recovery column is possible.

Graph 1



Graph 2

Thus, according to the invention, typically 90% of the olefins and paraffins are recovered from the liquid-liquid extraction column. The 10% of olefins and paraffins not recovered are sent to the solvent recovery column in the extract from the liquid-liquid extraction column. Up to 60% of the olefins and paraffins in the solvent recovery column are recovered in the overheads product from the solvent recovery column and recycled to the liquid-liquid extraction column. This results in an over-all recovery of olefins and paraffins of more than 90%.

With reference to the Figure, a liquid-liquid extraction process of the invention includes an extraction column 20. The fractionated condensation product of a low temperature Fischer-Tropsch reaction described above 14 is fed into the extraction column 20 at, or near, the bottom thereof and a solvent stream 21 comprising a mixture of methanol and water is fed into the extraction column 20 at or near the top thereof. The solvent stream 21 preferably comprises more than 5% by weight water. The solvent to feed ratio in the solvent stream is low, typically less than 1.5.

Raffinate 22 from the top of the extraction column 20, which includes olefins and paraffins and a small amount of solvent, enters a raffinate

stripper column 23 and a hydrocarbon product stream comprising more than 90% by weight olefins and paraffins and less than 0.2% by weight, preferably less than 0.02% by weight oxygenates exits as a bottoms product 24. The bottoms product 24, which shows an overall recovery of over 90% of the olefins and paraffins contains more than 20% by weight α-olefins and more than 70% by weight n-paraffins. Thus, the olefin content of the hydrocarbon product (which is intended for use in the production of linear alkyl benzene) has been preserved. A solvent comprising mainly methanol (more than 90% by weight) and low concentrations of water (less than 5% by weight) and olefins/paraffins (less than 5% by weight) exits as a tops product 25 and is returned to the solvent feed stream 21. If it is desired to recover the bottoms product 24 as a vapour stream, this can be done by taking a bottoms vapour stream from the column 20. The liquid product from the column 20 will then be a very small effluent stream.

An extract 26 is drawn from the bottom of the extraction column 20 and is fed to solvent recovery column 27. A tops product 29 from the solvent recovery column 27 comprises over 90% by weight methanol, and olefins and paraffins. Up to 60% of the olefins and paraffins from the extract 26 are recovered to the tops product 29. The tops product is then recycled to the solvent stream 21. The oxygenate content of the tops product 29 can be as low as 50 ppm, depending on the solvent to feed ratio used in the extraction column 20. A bottoms product 28 from the solvent recovery column 27 comprises mainly water, oxygenates and olefins/paraffins. This bottoms product 28 forms two liquid phases that can be decanted in a decanter 30. The organic phase is an oxygenate, olefin and paraffin stream 31, which leaves the process as a product. The aqueous phase is a stream 32, which is recycled to the extraction column 20. This stream 32 can either enter the extraction column at the top along with the solvent stream 21, or slightly lower down the column 20, to prevent the low amount of oxygenates that will be present in this stream from appearing in the raffinate stream 22.

As mentioned above, normally, a high-boiling solvent is preferred for liquid-liquid extraction because the solvent recovery steps after extraction requires less energy than will be the case for a low-boiling solvent. However, it has been found that a mixture of methanol and water, which is a low-boiling solvent, need not suffer from this drawback, because it can be effective at low solvent to feed ratios (this can be lower than 1 if the required oxygenate extraction is not too severe).

A study of the different azeotropes that exist between components in the feed and water would lead one to expect that it would not be possible to distil water overhead in the solvent recovery column 27 without azeotroping oxygenates overhead as well. Surprisingly, this turns out not to be the case. Methanol, which does not form azeotropes with any of the other species present, prevents the water/oxygenate azeotropes from distilling over at the same temperature as the paraffins and olefins. This appears to be due to an extractive distillation effect. Additionally, it is possible to distil the paraffins and olefins overhead, while recovering the oxygenates as a bottoms product. This has the effect of enhancing the overall paraffin and olefin recovery of the process, because the overheads 29 of the solvent recovery column 27 is recirculated to the extraction column 20, which means that the paraffins and olefins will be forced to leave the process in the product stream 24.

It is therefore possible to have a hydrocarbon stream 24 with a high overall recovery of olefins and paraffins, without the use of a counter solvent in the extraction column. In this mode of operation, all the methanol, and part of the water (10-50%) are also recovered in the overhead stream 29.

Although, as mentioned above, paraffins and olefins from the recovery column 27 are recirculated to the extraction column 20 in the overheads stream 29, it has been found that the quantity of the paraffins and olefins recovered to the overheads 29 of the solvent recovery column 27 is limited because, eventually, light-boiling oxygenates start appearing in the overheads 29 in quantities greater than 10ppm. This is because at low-

solvent to feed ratios in the extraction column 20, there is insufficient water and methanol in the solvent recovery column 27 to get a sufficient extractive distillation effect. Further, when operating in this way, the heavier boiling paraffins and olefins show up in the overheads stream 29 in only very small quantities. The recovery of the paraffins and olefins from the extract 26 to the overheads 29 is therefore not greater than approximately 30% for solvent to feed ratios of 1-1.25 in the extraction column 20.

High solvent to feed ratios in the extraction column 20 would ensure large amounts of methanol in the recovery column 27, which would improve the extractive distillation effect. However, it is preferred to have as low a solvent feed ratio as possible. The need for a high methanol content in the recovery column 27 is overcome partly by adding a side-draw stream 34 to the recovery column 27. Less than 5% of the feed to the recovery column 27 is removed in the side-draw 34. This side-draw 34 is higher than the feed point of the extract 26 and lower than the draw-off of the overheads 29 in the recovery column 27. Paraffins and olefins in the C₁₀-C₁₁ range are removed predominantly in the side-draw 34. There will also be oxygenates (predominantly light boiling ketones and aldehydes) in the side-draw 34 in small amounts. Methanol is still removed predominantly in the overheads 29. The main benefit of the side-draw 34 on the recovery column 27 is that the overheads 29 has very low quantities of oxygenates (less than 20ppm). The side-draw 34 is fed to a decanter 36 which separates an organic phase 38 which comprises, predominantly, paraffins and olefins in the C₁₀-C₁₁ range and a small amount of oxygenates (predominantly light boiling ketones and aldehydes). The stream 38 may be recycled to the broad cut 14. Although there are oxygenates present in this stream, they are tolerated in the broad cut 14. An aqueous phase 40 from the decanter 36 is recycled to the extraction column 20 via a stream 32 which is discussed below.

It is also possible to run the extraction column 20 and the solvent recovery column 27 at different methanol / water ratios. This may be desirable

because a high water content in the extraction column 20 will lead to increased solvent to feed ratios (because of reduced solubility of oxygenates in the solvent), while a certain amount of water is necessary to achieve the extractive distillation effect in combination with methanol to recover all the paraffins and olefins as overhead products in the solvent recovery column 27. The different methanol / water ratios in the two columns (20 and 27) can be achieved by diverting some of the water in stream 32 to stream 26 by means of a stream 33.

After passing the C₁₀ – C₁₃ hydrocarbon feed stream mentioned above through the abovementioned oxygenate extraction process using a mixture of methanol (95% by weight) and water (5% by weight) and a solvent to feed ratio of 1.25, the purified hydrocarbon feed stream contains 22% by weight olefins, 76% by weight paraffins and less than 0.02% by weight oxygenates. Not only does the extraction process extract oxygenates, it also preserves the olefin content of the hydrocarbon feed. The purified hydrocarbon feed stream containing olefins is particularly useful in the production of linear alkyl benzene.

The invention will now be described in more detail with reference to the following non-limiting examples.

Example 1

This example shows a process according to the invention without a side-draw to the solvent recovery column 27. The extraction column 20 was run at a solvent to feed ratio of 1.25 and a temperature of 50°C. The overall olefin/paraffin recovery in the stream 24 was 89.9%, with an α-olefin concentration of 21.6% by weight, n-paraffin concentration of 72.2% by weight and 0.3% by weight branched hydrocarbons and 5.9% by mass internal olefins.

Extraction column 20

Stream	14		21		22		26	
	Comp (wt%)	Flow (kg/hr)						
Total	100	3000	100	3750	100	2530	100	4220
Total C10-C13 P/O	92.7	2779.7	2.16	81.0	99.1	2507.9	6.20	261.7
Total Oxygenates	7.3	217.7	0.000	0.000	0.0144	0.365	5.78	243.7
Lights and Heavies	0.057	1.7	0.004	0.144	0.0104	0.263	0.00480	0.202
Water	0.031	0.934	6.01	225.6	0.0073	0.184	5.74	242.4
Methanol	0.000	0.000	91.7	3443.3	0.842	21.31	82.3	3472.0

Raffinate Stripper column 23

Stream	22		25		24	
	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)
Total	100	2530	100	30	100	2500
Total C10-C13 P/O	99.1	2507.9	2.63	0.793	99.97	2499.4
Total Oxygenates	0.0144	0.365	0.00163	0.000491	0.0145	0.363
Lights and Heavies	0.0104	0.263	0.0887	0.0267	0.00808	0.202
Water	0.0073	0.184	1.62	0.456	0.00115	0.0288
Methanol	0.842	21.31	95.4	28.7	0.000	0.000

Solvent Recovery column 27

Stream	26		29		28	
	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)
Total	100	4220	100	3584	100	636
Total C10-C13 P/O	6.20	261.7	2.37	85.1	27.6	175.8
Total Oxygenates	5.78	243.7	0.00140	0.0503	42.0	267.0
Lights and Heavies	0.00480	0.202	0.00747	0.268	0.00279	0.0177
Water	5.74	242.4	1.30	46.8	29.3	186.6
Methanol	82.3	3472.0	96.2	3451.9	1.04	6.63

Example2

This example shows a process according to the invention with a side-draw 34 to the solvent recovery column 27. The extraction column 20 was run at a solvent to feed ratio of 1.25 and a temperature of 50°C. The overall olefin/paraffin recovery in the stream 24 was 92.7%, with an α-olefin concentration of 21.6% by weight, n-paraffin concentration of 72.2% by weight and 0.3% by weight branched hydrocarbons and 5.9% by weight internal olefins.

Extraction column 20

Stream	14		21		22		26	
	Comp (wt%)	Flow (kg/hr)						
Total	100	3000	100	3750	100	2806	100	4144
Total C10-C13 P/O	92.7	2779.6	4.38487391	164.4	99.5	2592.7	8.5	350.8
Total Oxygenates	7.3	217.8	3.69E-03	0.139	0.0140	0.365	5.2510	217.6
Lights and Heavies	0.057	1.7	0.0061023	0.229	0.0642	1.672	0.0055	0.228
Water	0.031	0.93677517	4.59438605	172.3	0.0054	0.142	4.2231	175.0
Methanol	0.001	0.024	91.0109175	3412.9	0.426	11.09	82.056	3400.4

Raffinate Stripper column 23

Stream	22		25		24	
	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)
Total	100	2606	100	30	100	2576
Total C10-C13 P/O	99.6	2592.7	2.63	0.793	99.97	2575.4
Total Oxygenates	0.0140	0.365	0.00183	0.000491	0.0141	0.364
Lights and Heavies	0.0642	1.672	0.0867	0.0267	0.00808	0.208
Water	0.0054	0.142	1.62	0.456	0.00116	0.0296
Methanol	0.426	11.09	95.4	28.7	0.000	0.000

Solvent Recovery column 27

Stream	26		29		28		38		40	
	Comp (wt%)	Flow (kg/hr)								
Total	100	4144	100	3617	100	522	100	0.723	100	4.277
Total C10-C13 P/O	8.5	350.8	4.53	163.8	35.8	186.7	73.3	0.5	0.0	0.0
Total Oxygenates	5.2510	217.6	0.00127	0.0460	41.7	217.7	22.8	0.2	0.7	0.0
Lights and Heavies	0.0055	0.228	0.00630	0.228	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Water	4.2231	175.0	1.54	65.5	22.5	117.7	0.4	0.0	45.0	1.9
Methanol	82.056	3400.4	93.9	3397.4	0.00	0.00	3.32	0.02	54.24	2.32

CLAIMS

1. A method for extracting oxygenates from the hydrocarbon condensation product of a low temperature Fischer-Tropsch reaction, while preserving the olefin content of the hydrocarbon condensation product, the method including the step of extracting the oxygenates in a liquid-liquid extraction process using a mixture of methanol and water as the solvent.
2. The method according to claim 1 wherein an extract from the liquid-liquid extraction is sent to a solvent recovery column from which a tops product comprising methanol, olefins and paraffins is recycled to the extraction process.
3. The method according to claim 1, wherein, prior to extraction, the hydrocarbon condensation product contains 15% to 30% by weight olefins, 60% to 80% by weight paraffins and 5% to 10% by weight oxygenates.
4. The method according to claim 2, wherein the solvent in the liquid-liquid extraction comprises more than 3% by weight water.
5. The method according to claim 4, wherein the solvent in the liquid-liquid extraction comprises more than 5% to 15% by weight water.
6. The method according to claim 1, wherein liquid-liquid extraction process takes place in a liquid extraction column.
7. The method according to claim 6, wherein a raffinate from the extraction column is sent to a raffinate stripper column from which a hydrocarbon feed stream containing olefins and paraffins and less than 0.2% by weight oxygenates exits as a bottoms product.

8. The method according to claim 7, wherein a raffinate from the extraction column is sent to a stripper column from which a hydrocarbon feed stream containing olefins and paraffins and less than 0.02% by weight oxygenates exits as a bottoms product.
9. The method according to claim 7, wherein a tops product from the raffinate stripper is recycled to the extraction column.
9. A method according to claim 2 wherein the solvent recovery column includes an extract inlet, an upper overhead outlet and a lower bottoms outlet, with a side-draw located above the extract feed point and below the overheads outlet.

